PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-316711
(43)Date of publication of application : 02.12.1998

(51)Int.Cl. C08F 4/642
C08F210/00
C08F210/14
C08F212/00
C08F290/04
C08L 23/00
C08L 25/00
C08L 55/00
//(C08F290/04
C08F210:00)

(21)Application number : 10-058489
(22)Date of filing : 10.03.1998

(71)Applicant : BASF AG
(72)Inventor : ARNOLD MANFRED
HENSCHKE OLAF DR

(30)Priority
Priority number : 97 19709667 Priority date : 11.03.1997 Priority country : DE

(54) PRODUCTION OF COMB POLYMER IN THE PRESENCE OF METALLOCENE CATALYST

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a comb copolymer having a high molecular weight and a polymer chain having a uniform comonomer distribution by polymerizing at least one monomer being either an olefinically unsaturated 2-18 C hydrocarbon or a vinyl aromatic compound with at least either a long-chain 1-(20-40 C) alkene or a macromonomer in the presence of a metallocene catalyst.
SOLUTION: The olefinically unsaturated hydrocarbon monomer is ethylene, propylene, 1-butene, 1-hexene or norbornene among which propylene is particularly desirable. The vinyl aromatic compound monomer is desirably styrene, α-styrene, divinylbenzene or 2vinylnaphthalene. The long-chain 1-alkene is exemplified by 1eicosene. The macromonomer is desirably a vinyl- or vinylideneterminated oligomer. The monomer is suitably styrene, α methylstyrene, 2-vinylnaphthalene, 1,3-butadiene, isoprene or isobutylene. A compatibilizer for a polyblend can thus be obtained.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

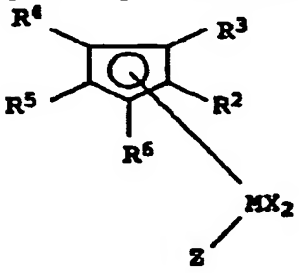
[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

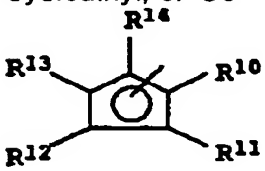
CLAIMS

[Claim(s)]
[Claim 1] The manufacturing method which is a manufacturing method of the Kushigata polymer which carries out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to one or more sorts of monomers b chosen from the long-chain 1-(C20-C40) alkene and the macro monomer under existence of a catalyst, and is characterized by using a metallocene catalyst as a catalyst.
[Claim 2] a metallocene catalyst -- as an active ingredient -- A type (III): -- [Formula 1]

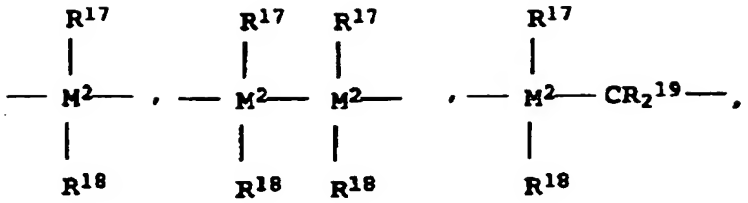


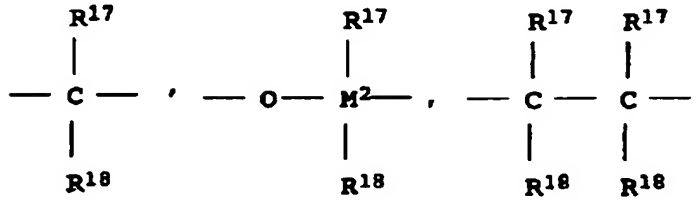
III

(M is titanium, a zirconium, a hafnium, vanadium, niobium, or a tantalum among a formula. X) Fluorine, chlorine, a bromine, iodine, hydrogen, C1 - C10 alkyl, C6 - C15 aryl, the alkyl aryl and -OR7 which have 6-20 carbon atoms in an alkyl group at 1-10 carbon atoms and an aryl group Or -NR seven R8 it is -- R7 And R8 Respectively C1 - C10 alkyl, C6 - C15 aryl, alkyl aryl, They are arylated alkyl, fluoro alkyl, or fluoro aryl. each radical -- an alkyl group -- 1-10 carbon atoms and an aryl group -- 6-20 carbon atoms -- having -- R2 -R6 Respectively Hydrogen, C1 - C10 alkyl, the cycloalkyl of 5 - 7 member (you may have C1 - C10 alkyl as a substituent), C6 - C15 aryl or arylated alkyl (two contiguity radicals may form the annular radical of the saturation of 4-15 carbon atoms, or partial saturation together), or Si (R9)3 it is -- R9 C1 - C10 alkyl, C3 - C10 cycloalkyl, or C6 - C15 aryl -- it is -- Z -- X or [Formula 2]

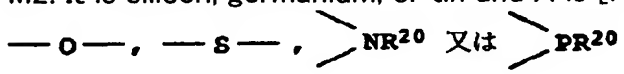


Come out and it is. R10-R14, respectively Hydrogen, C1 - C10 alkyl, The cycloalkyl of 5 which may have C1 - C10 alkyl as a substituent - 7 members, C6 - C15 aryl or arylated alkyl (two contiguity radicals may form the annular radical of the saturation of 4-15 carbon atoms, or partial saturation together), or Si (R15)3 it is -- R15 -- C1 - C10 alkyl, C6 - C15 aryl, or C3 - C10 cycloalkyl -- it is -- R5 [or] and Z -- together -- radical-R16-A- forming -- R16 -- [Formula 3]





= BR17, =AlR17, -germanium-, -Sn-, -O-, -S-, It is SO, =SO2, =NR17, =CO, =PR17, or =P(O) R17. = R17, R18, and R19 the same -- or -- differing -- respectively -- hydrogen, a halogen, and C1-C -- 10 alkyl C1 - C10 fluoro alkyl, C6 - C10 fluoro aryl, C6 - C10 aryl, C1 C10 alkoxy **C2 - C10 alkenyl, Two contiguity radicals form a ring together with [are C7 - C40 arylated alkyl, C8 - C40 aryl alkenyl, or C7 - C40 alkyl aryl or] the atom which combines them, and it is M2. It is silicon, germanium, or tin and A is [Formula 4].



coming out -- it is -- R20 -- C1 - C10 alkyl, C6 - C15 aryl, C3 - C10 cycloalkyl, alkyl aryl, or Si (R21)3 it is -- R21 They are hydrogen, C1 - C10 alkyl, C6 - C15 aryl (C1 -C4 alkyl may permute), or C3 - C10 cycloalkyl. R5 [or] R13 [and] -- together -- radical-R16- forming -- manufacturing method according to claim 1 characterized by containing the metallocene complex expressed and the compound which forms B meta-ROSENIUMU ion.

[Claim 3] The manufacturing method according to claim 1 or 2 characterized by using 1-(C2 - C10) alkene as a monomer a, and using a vinyl aromatic series macro monomer as a monomer b.

[Claim 4]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacturing method of the Kushigata polymer which carries out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to one or more sorts of monomers b chosen from the long-chain 1-(C20-C40) alkene and the macro monomer under existence of a catalyst. Moreover, this invention is the Kushigata polymer (a new Kushigata polymer is called hereafter) and the Kushigata polymer which are made to carry out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to the bottom of existence of one or more sorts of monomers b chosen from the long-chain 1-(C20-C40) alkene and the macro monomer and a catalyst, and are obtained as a compatibilizer of a polymer blend. It is related with the approach of using it, and the polymer blend (a new polymer blend is called hereafter) containing a new Kushigata polymer.
[0002]
[Description of the Prior Art] Mixing the pure polymer which has different physical properties, in order to acquire the desirable property of plastics is usually carried out in a plastics technique. However, much a pure polymer, for example, polyolefine, and polystyrene are not mixed to homogeneity for those different structures. generally the heterogeneous-polymerization object blend was inferior to the basic polymer of a blend -- it has mechanical and/or optical property. It is known that it can be increased by using a compatibilizer by the miscibility of a different polymer.
[0003] However, in order to make those functions, it is still impossible to predict the structure which a compatibilizer should hold.
[0004] Usually, the compatibilizer of the polyolefine / polystyrene blend of a non-polarity is not studied completely.
[0005] Copolymerization of the ethylene and the propylene under existence of a vanadium catalyst, and the macro monomer of alpha methyl styrene with an end allyl group is indicated by U.S. Pat. No. 3,989,768. However, this process has some fault. On the other hand, a vanadium catalyst is not fully productive. That is, the yield of a polymer is unsatisfying. Furthermore, ****** of the macro monomer to a polymer chain is not fully uniform, and especially the molecular weight of a copolymer has it. [in addition inadequate for applying to a polymer blend]
[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the Kushigata copolymer which can remove the above faults, it is the amount of giant molecules, and comonomer distribution of a polymer chain is uniform, fits the compatibilizer of a polymer blend, and can moreover be manufactured by the productive approach.
[0006]
[Means for Solving the Problem] We found out that such a technical problem was attained according to the manufacturing method of the Kushigata polymer which carries out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to the bottom of existence of one or more

sorts of monomers b and the metallocene catalyst which were chosen from the long-chain 1-(C20-C40) alkene and the macro monomer. Moreover, we found out the approach of using the Kushigata polymer which is made to carry out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to the bottom of existence of one or more sorts of monomers b and the metallocene catalyst which were chosen from the long-chain 1-(C20-C40) alkene and the macro monomer, and is obtained, and the Kushigata polymer as a compatibilizer of a polymer blend, and the polymer blend containing the Kushigata polymer.

[0007] A new Kushigata polymer has at least one principal chain of the limited die length which branches many side chains preferably.

[0008] In a new manufacturing method, such a Kushigata polymer carries out copolymerization of the monomer a which forms the principal chain of a new Kushigata polymer generally, and the long-chain monomer b which forms a side chain generally to the bottom of existence of a metallocene catalyst, and is obtained.

[0009] Using a metallocene catalyst, Monomers a are all monomers in which a polymerization is possible, and have the carbon-carbon double bond especially the vinyl, or the vinylidene mold of an end preferably.

[0010] the suitable monomer a -- annular -- or -- desirable -- a line -- they are olefin partial saturation [which has structure] C2 - C18 hydrocarbon, and C8 - C16 vinyl aromatic compound. the example of C2 - C18 hydrocarbon -- a line or annular C2 - C18 monomer and a line or annular C4 - C -- it is diene preferably 18 polyene.

[0011] Suitable olefin unsaturated hydrocarbon is 1-(C2 - C10) alkene, for example, ethylene, a propylene, 1-butene, isobutene, 1-hexene, 1-octene, 1-decene, cyclopentene, a cyclohexene, cyclooctane, norbornene, 1,3-butadiene, 1, 5-cyclo-octadiene, norbornadiene, 5-vinyl-2-norbornene, 5-phenyl-2-norbornene, and dimethano octahydro naphthalene.

[0012] The very desirable monomers a are ethylene, a propylene, 1-butene, 1-hexene, and norbornene.

[0013] The examples of a suitable vinyl aromatic compound are styrene, alpha methyl styrene, a divinylbenzene, and 2-vinyl naphthalene.

[0014] The desirable vinyl aromatic series monomer a is styrene.

[0015] Of course, the monomer a of a publication can also be used as mixture for copolymerization, and is not criticality-like [a mixing ratio] in this case. desirable mixture -- the monomer of a propylene and others of Group a -- it is mixture with ethylene, 1-butene, 1-hexene, 1-octene, or norbornene preferably.

[0016] However, the very desirable only monomer a is used for composition of a polymer principal chain, and especially a propylene is used as a monomer a.

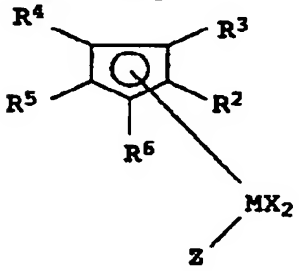
[0017] Monomer a and copolymerization under existence of a metallocene catalyst are possible for the suitable monomer b. Such a monomer has the thing of the carbon-carbon double bond of an end especially vinyl, or a vinylidene mold preferably. Generally the description which distinguishes Monomer b from Monomer a is the chain length or polymerization degree. Monomer b is usually the amount of macromolecules from Monomer a. Preferably, the molecular weight Mn of Monomer b is 3 to 2000 times as large as Monomer a.

[0018] The suitable monomer b is long-chain C 20 - C40 monoolefin, for example, 1-ray KOSEN.

[0019] However, especially the desirable monomer b consists of macro monomers, i.e., a monomer, and are the chain end section which can copolymerize functionality, and oligomer which has end vinyl or a vinylidene radical preferably.

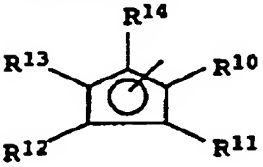
[0020] The monomer used as the foundation of a macro monomer may be chosen from Monomer a. Although a macro monomer may be the gay oligomer or co-oligomer of these monomers, it is gay oligomer preferably. The polymerization of the desirable monomer used as the foundation of a macro monomer is carried out by a cation or the living polymerization by which anion initiation is carried out. so, the suitable monomer b -- vinyl aromatic hydrocarbon -- they are styrene or alpha methyl styrene, 2-vinyl naphthalene, 1,3-butadiene, an isoprene, and an isobutylene preferably.

[0021] Isobutylenes are Polymer(s), such as J.P.Kennedy. A polymerization is carried out by living cationic polymerization and molecular weight 300-50000 and the polyisobutylene which has 1000 - 20000 g/mol preferably are usually produced so that it may be indicated after six volumes (1995) and 579 page. Thus, generally molecular-weight-distribution Mw/Mn of the polyisobutylene obtained is 1.05-2.0. The initiator to be used is 2-chloro. - You may be a 2, 4, and 4-trimethyl pentane, and a living polymerization object is made to usually react with the arylsilane as an organic-functions-ized agent for introducing a partial saturation end group, for example, an allyl compound trimethyl silane.
[0022] Styrene is indicated after M.Swarc, J.Am.Chem.Soc., 78 volumes, (1956), and 2656 page. A polymerization is usually carried out by living anionic polymerization by making for example, n-butyl lithium or sec.-butyl lithium into an initiator, and a polystyrene anion is generated. subsequently, a living polymer chain -- general -- molecular weight 300-Mn 50000 -- it has 1000 - 20000 g/mol and molecular-weight-distribution Mw/Mn 1.05-1.5 preferably, and is generally organic-functions-ized in the chain end section. For this reason, a living polystyrene anion is made to react generally with an electrophilicity allyl compound, a vinyl compound, for example, an allyl chloride, or chlorination vinylbenzyl.
[0023] average molecular weight Mw and Mn list -- molecular-weight-distribution Mw/Mn -- general -- elevated-temperature gel permeation chromatography (GPC) -- in 135 degrees C, it measures by law by the 1,2,4-trichlorobenzene which has polystyrene as a reference material. A new polymerization method is enforced under existence of a metallocene catalyst. A metallocene catalyst means the catalytic activity transition-metals compound which has at least one sort of ligands drawn from at least one sort of cyclopentadienyl ligands, or a cyclopentadienyl structural unit. Usually, a catalyst contains the compound which forms a metallocene cation and this compound is also called cocatalyst.
[0024] Especially the suitable metallocene complex used as the foundation of a metallocene catalyst is Formula III. [0025]
[Formula 9]



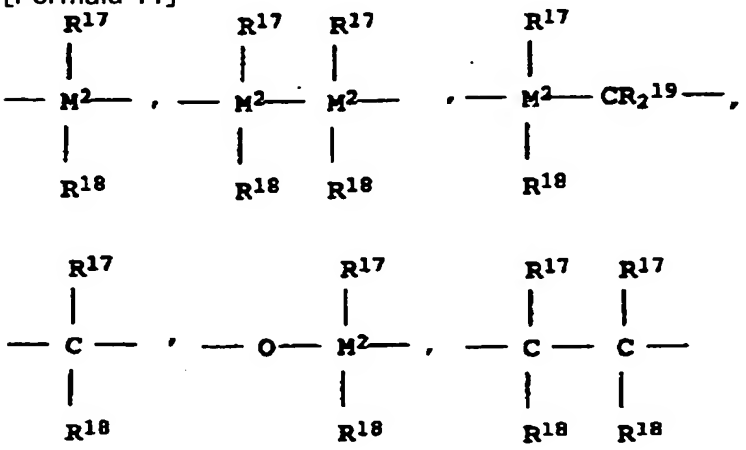
III

(M is titanium, a zirconium, a hafnium, vanadium, niobium, or a tantalum among a formula. X) Fluorine, chlorine, a bromine, iodine, hydrogen, C1 - C10 alkyl, C6 - C15 aryl, the alkyl aryl and -OR7 which have 6-20 carbon atoms in an alkyl group at 1-10 carbon atoms and an aryl group Or -NR seven R8 it is -- R7 And R8 Respectively C1 - C10 alkyl, C6 - C15 aryl, alkyl aryl, They are arylated alkyl, fluoro alkyl, or fluoro aryl. each radical -- an alkyl group -- 1-10 carbon atoms and an aryl group -- 6-20 carbon atoms -- having -- R2 -R6 Respectively Hydrogen, C1 - C10 alkyl, the cycloalkyl of 5 - 7 member (you may have C1 - C10 alkyl as a substituent), C6 - C15 aryl or arylated alkyl (two contiguity radicals may form the annular radical of the saturation of 4-15 carbon atoms, or partial saturation together), or Si (R9)3 it is -- R9 C1 - C10 alkyl, C3 - C10 cycloalkyl, or C6 - C15 aryl -- it is -- Z -- X -- or [0026]
[Formula 10]

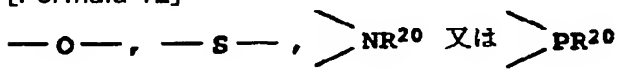


Come out and it is. R10-R14, respectively Hydrogen, C1 - C10 alkyl, The cycloalkyl of 5 which

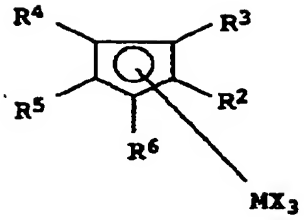
may have C1 - C10 alkyl as a substituent - 7 members, C6 - C15 aryl or arylated alkyl (two contiguity radicals may form the annular radical of the saturation of 4-15 carbon atoms, or partial saturation together), or Si (R15)3 it is -- R15 -- C1 - C10 alkyl, C6 - C15 aryl, or C3 - C10 cycloalkyl -- it is -- R5 [or] and Z -- together -- radical-R16-A- forming -- R16, [0027]
[Formula 11]



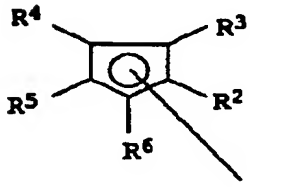
= BR17, =AlR17, -germanium-, -Sn-, -O-, -S-, It is SO, =SO2, =NR17, =CO, =PR17, or =P(O) R17. = R17, R18, and R19 the same -- or -- differing -- respectively -- hydrogen, a halogen, and C1-C -- 10 alkyl C1 - C10 fluoro alkyl, C6 - C10 fluoro aryl, C6 - C10 aryl, C1 C10 alkoxy **C2 - C10 alkenyl, Two contiguity radicals form a ring together with [are C7 - C40 arylated alkyl, C8 - C40 aryl alkenyl, or C7 - C40 alkyl aryl or] the atom which combines them, and it is M2. It is silicon, germanium, or tin and is A, [0028]
[Formula 12]



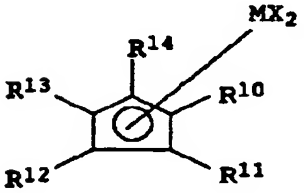
coming out -- it is -- R20 -- C1 - C10 alkyl, C6 - C15 aryl, C3 - C10 cycloalkyl, alkyl aryl, or Si (R21)3 it is -- R21 hydrogen, C1 - C10 alkyl, C6 - C15 aryl (C1 -C4 alkyl may permute), or C3 - C10 cycloalkyl -- it is -- R5 [or] R13 [and] -- together -- radical-R16- forming -- it is the metallocene complex expressed.
[0029] Inside of the metallocene complex of Formula III, [0030]
[Formula 13]

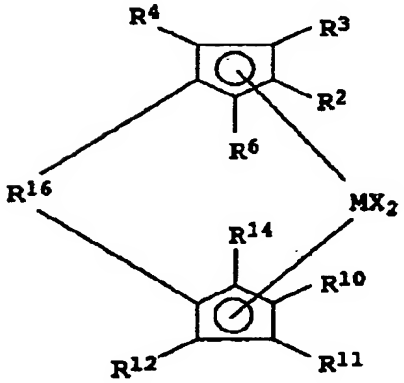


IIIa

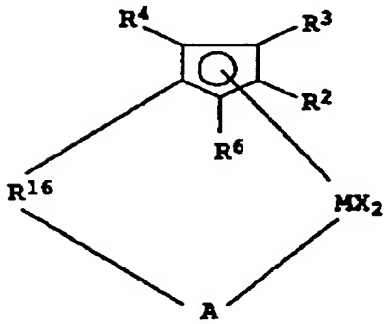


IIIb,





IIIc 及び



IIId

** -- it is desirable.

[0031] that in which especially a desirable transition metal complex contains as a ligand two aromatic ring systems over which the bridge was constructed mutually -- that is, it is especially the transition metal complex of Formulas IIIc and IIId.

[0032] The same thing is desirable although it is that Radical X is the same or a different thing.

[0033] M of especially the desirable compound of Formula IIIa is titanium, a zirconium, or a hafnium, and X is chlorine, and C1 - C4. It is alkyl or phenyl and is R2 -R6. They are hydrogen, or C1 - C4, respectively. It is alkyl.

[0034] especially the desirable compound of Formula IIIb -- M -- titanium, a zirconium, or a

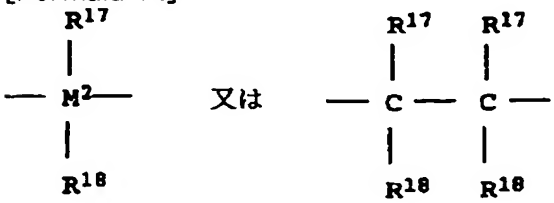
hafnium -- it is -- X -- chlorine, and C1 - C4 alkyl or phenyl -- it is -- R2 -R6 respectively -- hydrogen, and C1 - C4 Alkyl or Si (R9)3 it is -- R10-R14 -- hydrogen, and C1 - C4 Alkyl or Si (R15)3 it is -- it is a thing.

[0035] Especially the suitable compound of Formula IIIb has the same cyclopentadienyl group.

[0036] : in which especially the example of a suitable compound contains the following -- they are screw (cyclopentadienyl) zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, screw (methylcyclopentadienyl) zirconium dichloride, screw (ethylcyclopentadienyl) zirconium dichloride, screw (n-butylcyclopentadienyl) zirconium dichloride, bis (trimethylsilylcyclopentadienyl)zirconiumdichloride, and a corresponding dimethyl zirconium compound.

[0037] Especially the suitable compound of Formula IIIc is R2. R10 [and] It is the same, is hydrogen or C1 - C10 alkyl, respectively, and is R6. R14 [and] It is the same and they are hydrogen, methyl, ethyl, isopropyl, or tert.-butyl, respectively. R4 R12 [and] -- respectively -- C1 - C4 Alkyl and R3 R11 [and] -- respectively -- one [hydrogen or two contiguity radicals, and] R3 And R4 the annular radical to which R11 and R12 of another side have 4-12 carbon atoms together in a list -- forming -- R16, [0038]

[Formula 14]

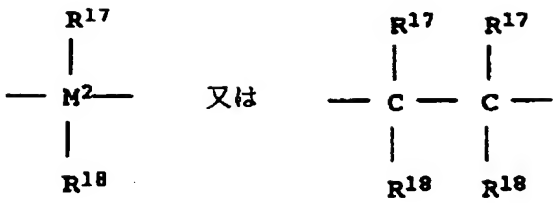


Come out, it is, M is titanium, a zirconium, or a hafnium, and X is chlorine, and C1 - C4. They are alkyl or phenyl.

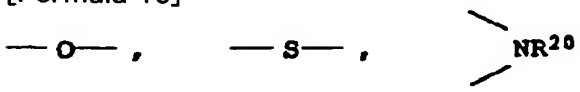
[0039] : in which especially the example of a suitable complex compound contains the following -- dimethylsilane diyl screw (cyclopentadienyl) zirconium dichloride -- Dimethylsilane diyl screw (indenyl) zirconium dichloride, Dimethylsilane diyl screw (tetrahydro indenyl) zirconium dichloride, Ethylene screw (cyclopentadienyl) zirconium dichloride, ethylene screw (indenyl) zirconium dichloride, Ethylene screw (tetrahydro indenyl) zirconium dichloride, Tetramethyl ethylene-9-fluorenyl cyclopentadienyl zirconium dichloride, Dimethylsilane diyl screw (3-tert.-butyl-5-methylcyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (3-tert.-butyl-5-ethylcyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (2-methyl indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-isopropyl indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-tert.-butyl indenyl) zirconium dichloride, Diethylsilane diyl screw (2-methyl indenyl) zirconium jib ROMIDO Dimethylsilane diyl screw (3-methyl-5-methylcyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (3-ethyl-5-isopropyl cyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (2-methyl indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-methyl bends indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-ethyl bends indenyl) zirconium dichloride, Methylphenyl silane diyl screw (2-ethyl bends indenyl) zirconium dichloride, Methylphenyl silane diyl screw (2-methyl bends indenyl) zirconium dichloride, Diphenyl silane diyl screw (2-methyl bends indenyl) zirconium dichloride, They are diphenyl silane diyl screw (2-ethyl bends indenyl) zirconium dichloride, dimethylsilane diyl screw (2-methyl indenyl) hafnium dichloride, and a corresponding dimethyl zirconium compound.

[0040] M of especially the suitable compound of Formula IIId is titanium or a zirconium, and X is chlorine, and C1 - C4. It is alkyl or phenyl and R16 , [0041]

[Formula 15]

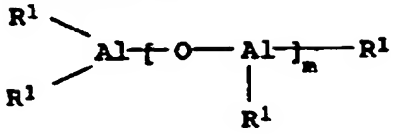


Come out, and it is and is A, [0042]
[Formula 16]

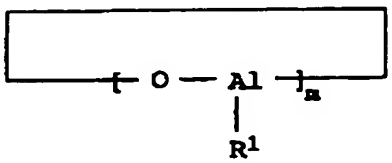


Come out, and it is and is R2 -R4. And R6 Hydrogen, C1 - C10 alkyl, C3 - C10 cycloalkyl, C6 - C15 aryl, Si (R9)3, or two contiguity radicals form the annular radical of 4-12 carbon atoms, respectively.
[0043] the cyclic hydrocarbon which could perform composition of such a complex compound by the well-known approach, and was permuted suitably -- Anio -- a reaction with the halogenide of Inn, titanium, a zirconium, a hafnium, vanadium, niobium, or a tantalum is desirable.
[0044] The example of a suitable manufacturing method is divided and is indicated by J.Organometal.Chem.369 (1989), and 359-370.
[0045] The mixture of a different metallocene complex may be used.
[0046] The catalyst manufactured according to a new manufacturing method contains a meta-ROSENIUMU ion formation compound as further component.
[0047] A suitable meta-ROSENIUMU ion formation compound is an ion compound which has Broensted acid as the ion compound and cation which have strong, neutral Lewis acid and a Lewis acid cation.
[0048] Strong, neutral desirable Lewis acid A formula IVM 3X1X2X3 IV (it is B preferably the inside of a formula, and M3 -- the III main-group element of a periodic table -- especially -- B, aluminum, or Ga -- X1, X2, and X3) Respectively Hydrogen, C1 - C10 alkyl, C6 - C15 aryl, Alkyl aryl, arylated alkyl, halo alkyl, or halo aryl (each radical has 6-20 carbon atoms in an alkyl group at 1-10 carbon atoms and an aryl group), or fluorine, chlorine, a bromine or iodine, especially halo aryl -- desirable -- pentafluorophenyl -- it is -- it is the compound expressed.
[0049] especially the compound of the desirable formula IV -- X1 and X2 And X3 the same thing -- it is tris (pentafluorophenyl) borane preferably.
[0050] The suitable ion compound which has a Lewis acid cation is formula V[(Ya+) Q1 Q2... Qz] d+ V (Y is the element of the I-VI main group of a periodic table, or an I-VIII vice-group among a formula Q1 -Qz) The radical which has a respectively single negative charge, for example, C1 - C28 alkyl, C6 - C15 aryl, alkyl aryl, arylated alkyl, halo alkyl, or halo aryl (each radical has 1-28 carbon atoms in an aryl group at 6-20 carbon atoms and an alkyl group), C1 - C10 cycloalkyl which may be permuted by C1 - C10 alkyl group, or -- although are a halogen, C1 C28 alkoxy **C6 - C15 aryloxy, silyl, or mel KAPUCHIRU, a is the integer of 1-6, z is the integer of 0-5 and d is equivalent to difference a-z -- d -- 1 -- stride -- 1 -- being equal -- it is the compound expressed.
[0051] A carbonium cation, an oxonium cation, a sulfonium cation, and especially a cation transition metal complex are suitable. A triphenylmethyl cation, silver cation and 1, and 1'-dimethyl ferro SENIRU cation is a special example. these have the opposite ion of non-coordination preferably, and are indicated by especially the PCT international public presentation WO 91/No. 09882 -- as -- a boron compound -- it is tetrakis (pentafluorophenyl) borate preferably.
[0052] The Broensted acid as a cation and the ion compound which has the opposite ion of non-coordination preferably are indicated by the PCT international public presentation WO 91/No. 09882, and a desirable cation is N and N-dimethyl anilinium.
[0053] Especially suitable meta-ROSENIUMU ion formation compounds are Formulas I or II.
[0054]

[Formula 17]



I



II

(-- the inside of a formula, and R1 -- C1 -C4 alkyl -- desirable -- methyl or ethyl -- it is -- m -- 5-30 -- it is the integer of 10-25 preferably --) -- they are the letter of opening and closing expressed, or an annular aluminoxane compound.

[0055] Manufacture of such aluminoxane compound oligomer makes a trialkylaluminium solution and water usually react. This divides and is indicated by the Europe patent application public presentation No. 284708 and U.S. Pat. No. 4,794,096.

[0056] Generally, aluminoxane compound oligomer exists as mixture of the line and annular chain molecule with which chain length differs. So, m can be called average. the metal alkyl of others [compound / aluminoxane] -- you may be mixture with alkylaluminum preferably.

[0057] Furthermore, aryloxy aluminoxane (U.S. Pat. No. 5,391,793 publication), amino aluminoxane (U.S. Pat. No. 5,371,260 publication), amino aluminoxane hydrochrolide (the Europe patent application public presentation No. 633264 publication), silyloxy aluminoxane (the Europe patent application public presentation No. 621279 publication), or such mixture may be used as a meta-ROSENIUMU ion formation compound.

[0058] Especially desirable metallocene complexes are ethylene screw (indenyl) hafnium dichloride and dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride. Very desirable metallocene catalysts are ethylene (bis-indenyl) hafnium dichloride / methyl aluminoxane, and dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride / methyl aluminoxane catalyst.

[0059] the new manufacturing method of the Kushigata polymer by this invention -- generally -- 50-300 degrees C -- desirable -- 0-150 degrees C -- especially -- 0-100 degrees C, and 0.01-3000 -- desirable -- 0.1-100 -- it carries out by 0.1-50 bars especially.

[0060] A polymerization can be performed by the solution, suspension, the liquid monomer, or the gaseous phase. A polymerization is preferably performed by the solution or the liquid monomer. The suitable solvent of solution polymerization is aliphatic series or an aromatic series organic solvent, and this may be halogenated. Toluene, ethylbenzene, a chlorobenzene, and a heptane are mentioned as an example.

[0061] A new polymerization method can be performed with a continuous magnetization method or a batch method. many stirring iron pots (reaction machine cascade) by which the suitable reaction machine was connected including the consecutive operation type stirring iron pot -- a tubular reaction machine or a loop-formation-like reaction machine is also still more possible.

[0062] The ratio of the monomer a opposite monomer b under polymerization is not criticality-like. general -- the mole ratio of the monomer a whole-quantity pair monomer b whole quantity -- 0.1-100 -- it is preferably chosen as 1-50.

[0063] the invert ratio of Monomer b -- usually -- 1-100 -- it is 5 - 90 % of the weight preferably. the rate of Monomer b that the chemical bond of [in a new Kushigata polymer] was carried out asks for the area under the curve obtained to the Kushigata polymer by the elevated-temperature gel-permeation-chromatography method as compared with the area of the homopolymer standard substance -- having -- 0.5-90 -- it is 5 - 75 % of the weight preferably.

[0064] the average molecular weight Mw and Mn list of a new Kushigata polymer -- molecular-weight-distribution Mw/Mn -- general -- elevated-temperature gel permeation chromatography (GPC) -- it asks at 1,2,4-trichlorobenzene and 135 degrees C by law, using polystyrene as a

reference material.
[0065] the average molecular weight Mw of a new Kushigata polymer -- generally -- 5000-1 million -- it is 10000 - 500000 g/mol preferably. molecular-weight-distribution Mw/Mn of a new copolymer -- usually -- 1.4-10 -- it is 1.4-3 preferably.
[0066] the glass transition temperature from which the melting point is 80-155 degrees C preferably, and one glass transition temperature or a large number usually separated 20-160 degrees C of new Kushigata polymers -100-250 degrees C of two separated glass transition temperature are -70-100 degrees C (it measures by the differential scanning calorimetry and DSC) preferably.
[0067] A very desirable new Kushigata polymer has one of the side chains of a polypropylene principal chain and polystyrene, or a polyisobutylene. the molecular weight Mw of this copolymer -- 5000-1 million -- desirable -- the molecular weight Mn of 10000 - 500000 g/mol and a side chain -- 500-50000, and the molecular weight distribution of a macro monomer that serve as a foundation of 2000 - 20000 g/mol and a side chain preferably -- usually -- 1.05-2.0 -- it is 1.05-1.4 preferably. the number of graft branching which the side chain of the Kushigata polymer reached comparatively and was calculated from the total molecular weight Mn of a desirable new Kushigata polymer -- the rate of 0.05-50, the macro monomer polystyrene by which is 1-20 preferably and the chemical bond was carried out, or a polyisobutylene -- 0.5-90 -- it is 5 - 75 % of the weight preferably.
[0068] The desirable new Kushigata polymer which has the side chain of a polypropylene principal chain and polystyrene, or a polyisobutylene usually has 120-155 degrees C and the glass transition temperature of -70-100 degrees C preferably the melting point of 100-160 degrees C.
[0069] Furthermore, although a new Kushigata polymer contains sheep inversion monomer b5-50 % of the weight to the total amount of polymers, it is desirable that Monomer b is not included substantially.
[0070] A new Kushigata polymer is applicable to the polymer blend which consists of two or more sorts of components as a compatibilizer. All polymers, i.e., thermoplastics resin, for example, polyolefine, polystyrene, a polyamide, polyester, a polycarbonate, polyvinyl chloride and an elastomer, for example, a polyisobutylene, polybutadiene, and polyisoprene can be used as a component of a polymer blend in principle. A new Kushigata polymer is used in favor of the polymer blend containing the polymer blend containing a nonpolar hydrocarbon polymer especially an olefin polymer, and polyvinyl aromatic series. Suitable polyolefine is the homopolymer of a propylene, a copolymer, or a polyisobutylene at a polyethylene mold like HDPE, LLDPE, or LDPE, and a pan. To this contractor, it is well-known, for example, these polymers are Ullmann's. Encyclopedia of Industrial It is indicated by Chemistry, 21 volumes, 487-577 pages, and VCH (1992). The special example of polyvinyl aromatic series is the homopolymer or copolymer of styrene well-known to this contractor, or alpha methyl styrene similarly. What has the side chain of a new Kushigata polymer especially a polypropylene principal chain and polystyrene, or a polyisobutylene is especially used for the polymer blend containing a propylene polymer especially a propylene homopolymer and a styrene polymer, especially a styrene homopolymer preferably.
[0071] The ratio of the basic polymer of a polymer blend is not criticality-like generally. the case of the polymer blend containing a propylene polymer and a styrene polymer -- a ratio -- 1-99 -- it is 5 - 20 % of the weight preferably. [for example,]
[0072] In the blend which consists of a polymer blend especially a propylene polymer, and a styrene polymer, although it has the side chain of a new Kushigata polymer especially a polypropylene principal chain and polystyrene, or a polyisobutylene, a content is not criticality-like. it -- the whole quantity of a basic polymer -- receiving -- usually -- 0.001-50 -- it is 0.2 - 20 % of the weight preferably.
[0073] Furthermore, a new polymer blend can contain the amount of common use of the usual additive known in PURASUCHIKUSU industry.
[0074] Generally a new Kushigata polymer brings about the improvement of whenever [rigidity / of the test piece especially created from the new polymer blend /, tensile strength, and/or

breaking extension].
[0075] (Example)
A) Styrene 19.4ml (169mmol) newly distilled to styrene 18ml (157mmol) and the macro monomer SO which were newly distilled to manufacture desiccation toluene 200ml of a styrene macro monomer and the macro monomer SI which have the manufacture example 1 end vinyl group of a macro monomer was introduced into the desiccation flask washed by the argon style.
[0076] Subsequently, several drops of 2M toluene solutions of sec.-butyl lithium were added at 25 degrees C until the thin color would be in the stable state. Then, 2ml of initiator solutions was added.
[0077] Mixture was cooled at -78 degrees C 1 hour after, and it diluted with THF100ml. and toluene 100ml similarly cooled by -78 degrees C in the living poly anion solution -- it added in 7ml (80mmol) of inside allyl bromides, and the solution of THF100ml.
[0078] The 16.3g polystyrene SI (Mn=4000 g/mol, Mw/Mn=1.08) completely formed into allyl compound organic functions and 17.5g SO were obtained.
[0079] The property of the generated styrene macro monomer is shown in Table 1.
[0080] The manufacture desiccation flask of the isobutylene macro monomer which has an example 2 end vinyl group was washed by the argon style, and 250ml [of desiccation methylene chlorides], 2, and 2'-bipyridyl 0.75g (4.5mmol) and desiccation n-hexane 350ml were introduced. Subsequently, mixture was cooled at -78 degrees C.
[0081] After 12ml (0.11 mols) of titanium tetrachlorides, and 5 minutes, 2in 6ml of methylene chlorides-chloro - 10ml (2, 4, and 4-trimethyl pentane 1.5g and n-hexane 9ml (6.75mmol)) of solutions was added. Then, 71ml (51.3g) was dropped to isobutene 44ml (31.7g) and the macro monomer IBII to the macro monomer IBI.
[0082] after [10 minutes] and allyl compound trimethyl silane 5g (43mmol) -- adding -- further -- methanol 50ml was added after 30 minutes.
[0083] 31g Polyisobutylene IBI (Mn=4700 g/mol, Mw/Mn=1.16) and the 50g macro monomer IBII which were completely formed into allyl compound organic functions were obtained after processing.
[0084] The property of the generated isobutylene macro monomer is shown in Table 1.
[0085]
[Table 1]
表1：

末端ビニル基を有するポリスチレンおよびポリイソブチレンのマクロモノマー

記号[a]	M_n (g/mol)	M_w (g/mol)	M_w/M_n	末端基	官能価 (%)
SO	4300	4600	1.06	ビニルベンジル[b]	> 95
SI	4000	4400	1.08	アリル	> 95
IBI	4700	5500	1.16	アリル	> 95
IBII	7600	9300	1.23	アリル	> 95

a) S= polystyrene macro monomer IB= polyisobutylene macro monomer b PSLi is made to react with chlorination vinylbenzyl and it is Composition c. The end group functional value of a polystyrene macro monomer measured and asked for the signal reinforcement of an end double bond proton, and the signal reinforcement of the methyl proton of the initiator radical of a chain start point by 1 H-NMR spectroscopy.
[0086] B) The 0.5l. reactor of the propylene and styrene macro monomer under existence of the manufacture example 3 dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride / methyl aluminoxane of a new Kushigata polymer which carried out copolymerization desiccation was washed by the argon style, and was filled with 20-degree C desiccation toluene 200ml.
[0087] Then, 1.9ml (equivalent to aluminum of 3.3mmol and molar mass 1000 g/mol by cryoscopic-method measurement) of toluene solutions of methyl aluminoxane and macro

monomer SI2.5g (equivalent to 0.625mmol) subsequently to desiccation toluene 50ml dissolved were added with the argon gage pressure of 0.3 bars.
[0088] The dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride dissolved in 1ml of toluene solutions of methyl aluminoxane was put for 2 hours, preliminary activation was carried out, and it added behind. Refer to Table 2 for the amount of metallocene chloride. Then, it decompressed, the argon was removed and propene ** was set as 0.1 bars. By suitable propene supply, the pressure under polymerization was held to 0.1 bars, and temperature was held at 20 degrees C.
[0089] It obtained with the yield which shows the Kushigata polymer in Table 2.
[0090] An experimental result is shown in Table 2.
[0091]
[Table 2]

表 2:

ポリプロピレン主鎖およびポリスチレングラフト鎖を有するグラフト共重合体

記号 a)	メタロセン濃度 *10-5, (mol/l)/ (メタロセンジクロリド (mg))]	マクロモノマー 転化率 (%)	マクロモノマー 含有量 b) (重量%)	M_w (kg/mol)	M_w/M_n	グラフト鎖数 n_g/ 分子	M_{nPP} c) (kg/mol)	T_m (°C)	収量 [g]
GSO d)	3.3 (4.2)	> 85	7	13.6	2.6	0.085	5	-	4.4
GSI1	4 (5.8)	24.3	7	310	2.46	2.1	41	153.4	5.6
GSI2	2 (2.9)	49.4	20	158	2.16	3.5	16	151.9	8.9
GSI3	8 (11.6)	34.7	40	44.1	1.44	2.9	8	144.4	3.5
GSI4	2 (2.9)	26.2	72	22.6	1.4	2.84	4	122.2	3.0

a) 記号：G＋マクロモノマーの記号＋試料No.

b) グラフト共重合体中のポリスチレン含有量

c) 2つのグラフト鎖間のポリプロピレン列の平均分子量

$M_{nPP} = (M_{n全体} - n_g \cdot M_{nマクロモノマー})/(n_g + 1)$

d) 触媒系エチレンビス（インデニル）ハフニウムジクロリド／メチルアルミノキサン、重合温度50℃、SOマクロモノマー0.85g（表1参照）

[0092] The 0.5l. reactor of the propylene and isobutylene macro monomer under existence of example 4 dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride / methyl aluminoxane which carried out copolymerization desiccation was washed by the argon style, and was filled with 20-degree C desiccation toluene 200ml.

[0093] Then, 8.3g (equivalent to 1.09mmol) of 1.9ml (equivalent to aluminum of 3.3mmol and molar mass 1000 g/mol by cryoscopic-method measurement) of toluene solutions of methyl aluminoxane and the macro monomer IBII subsequently to desiccation toluene 50ml dissolved was added with the argon gage pressure of 0.3 bars.

[0094] 2.9mg of the dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride dissolved in 1ml of toluene solutions of methyl aluminoxane was put for 2 hours, preliminary activation was carried out, and it added behind.
[0095] Then, it decompressed, the argon was removed and it was set as 0.15 bar of propene **.
[0096] By suitable propene supply, the pressure under polymerization was held to 0.15 bars, and temperature was held at 20 degrees C.
[0097] 12.0g of a copolymer GIBII1 was obtained.
[0098] The copolymer GIBII2 was similarly manufactured by 0.1-bar propene **.
[0099] Furthermore, the copolymer GIBI1 was manufactured by 0.2 bar of propene ** using 12.8g (2.7mmol) of the macro monomer IBI, and the copolymer GIBI2 was manufactured by 0.1 bar of propene **. Furthermore, for details, refer to Table 3.
[0100] An experimental result is shown in Table 3.
[0101]
[Table 3]

表 3：

ポリプロピレン主鎖およびポリイソブチレングラフト鎖を有するグラフト共重合体

記号 a)	プロペン圧 (bar)	マクロモノマー 転化率 (%)	マクロモノマー 含有量 b) (重量%)	M_w (kg/mol)	M_w/M_n	グラフト分枝数 n_g/分子	M_{nPP} c) (kg/mol)	T_m (°C)	収量 [g]
GIBI1	0.2	11.0	24	114	2.1	2.95	17	147.6	17.6
GIBI2	0.1	32.8	51	61	1.73	3.25	8	143.5	14.6
GIBII1	0.15	6.0	15	103	1.75	1.1	28	148.4	12.0
GIBII2	0.1	7.2	14	42	1.43	0.52	19	149.9	11.2

a) 記号：G＋マクロモノマーの記号＋試料No.

b) グラフト共重合体中のポリイソブチレン含有量

c) 2つのグラフト鎖間のポリプロピレン列の平均分子量

$M_{nPP} = (M_{n全体} - n_g \cdot M_{nマクロモノマー})/(n_g + 1)$

[0102] C) Manufacture gay polypropylene PS-S134 (Mw213000, Mn94000, Mw/Mn2.27) (it used as a basic polymer.) of polypropylene / polystyrene / Kushigata polymer blend Shell KF6100H (Mw324000, Mn72000, Mw/Mn4.5) and gay polystyrene Buna These were used by the ratio of 85 % of the weight of polypropylene, and 15 % of the weight of polystyrene.

[0103] The polypropylene principal chain and the polystyrene side chain, and the new Kushigata polymer with which standard polystyrene graft chain length has the content from which Mn4000** differs were manufactured like the example 3, and it was used in a various amount by

using this Kushigata polymer as a compatibilizer. Furthermore, for details, refer to Table 4.
[0104] The blend of a basic polymer and the Kushigata polymer was manufactured as follows.
[0105] Polypropylene and polystyrene were mixed in 180 degrees C by the ratio which had the granular thing calculated at the kneading room of the Brabender plastometer (content of 24g) for 15 minutes.
[0106] It adds to a suitable quantity of a compatibilizer, and is Irganox. 0.4 % of the weight of stabilizer mixture containing B225, J3025 (Ciba-Geigy make) 25%, and 50% of Jonol was beforehand added in the granular object.
[0107] The piece of a polymer blend blank test was manufactured, and the following quality of polymerization somatic was measured by the following approaches.
[0108]
It is ductility at the time of fracture by the tension test method of the tensile strength DIN 53455 by the tension test method of the elastic modulus DIN 53455 by the tension test method of DIN53455. [0109]
[Table 4]

表 4：

新規櫛形重合体で相溶化されたポリプロピレン／ポリスチレンブレンド85／15の機械的性質

記号	グラフト共重合体				ブレンドの性質		
	M_w (kg/mol)	グラフト鎖数／分子	ポリスチレン含有量 (%)	ブレンド中の割合 (%)	弾性率 (MPa)	σ_{max} a) (N/mm^2)	ε_R b) (%)
B10	-	-	-	0	1197	28.68	18.0
BG1	13.6	0.085	7	1	1300	31.80	10.5
BG2	13.6	0.085	7	3	1206	29.38	9.6
BG3	13.6	0.085	7	5	1181	32.12	8.7
BG4	310	2.1	7	1	1516	35.02	8.1
BG5	310	2.1	7	2.5	1472	36.02	6.2
BG6	310	2.1	7	4	1545	37.33	6.6
BG7	310	2.1	7	8	1564	38.63	4.6
BG8	158	3.5	20	1	1418	35.28	5.6
BG9	158	3.5	20	2.5	1476	39.78	6.4
BG10	44.1	2.9	40	0.5	1330	36.01	6.1
BG11	44.1	2.9	40	1.5	1274	36.79	7.3
BG12	22.6	2.84	72	1	1174	32.84	6.1

a) 引張強度　　b) 破断時伸度

[0110] The mere small quantity of the new Kushigata polymer compatibilizer under blend of bringing about the substantial increment in ductility at the time of rigidity, tensile strength, and fracture, for example, 1%, is clear. This showed the improvement of interphase adhesion and was found out by the morphological research using a scanning electron microscope.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] This invention relates to the manufacturing method of the Kushigata polymer which carries out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to one or more sorts of monomers b chosen from the long-chain 1-(C20-C40) alkene and the macro monomer under existence of a catalyst. Moreover, this invention is the Kushigata polymer (a new Kushigata polymer is called hereafter) and the Kushigata polymer which are made to carry out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to the bottom of existence of one or more sorts of monomers b chosen from the long-chain 1-(C20-C40) alkene and the macro monomer and a catalyst, and are obtained as a compatibilizer of a polymer blend. It is related with the approach of using it, and the polymer blend (a new polymer blend is called hereafter) containing a new Kushigata polymer.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] Mixing the pure polymer which has different physical properties, in order to acquire the desirable property of plastics is usually carried out in a plastics technique. However, much a pure polymer, for example, polyolefine, and polystyrene are not mixed to homogeneity for those different structures. generally the heterogeneous-polymerization object blend was inferior to the basic polymer of a blend -- it has mechanical and/or optical property. It is known that it can be increased by using a compatibilizer by the miscibility of a different polymer.
[0003] However, in order to make those functions, it is still impossible to predict the structure which a compatibilizer should hold.
[0004] Usually, the compatibilizer of the polyolefine / polystyrene blend of a non-polarity is not studied completely.
[0005] Copolymerization of the ethylene and the propylene under existence of a vanadium catalyst, and the macro monomer of alpha methyl styrene with an end allyl group is indicated by U.S. Pat. No. 3,989,768. However, this process has some fault. On the other hand, a vanadium catalyst is not fully productive. That is, the yield of a polymer is unsatisfying. Furthermore, ****** of the macro monomer to a polymer chain is not fully uniform, and especially the molecular weight of a copolymer has it. [in addition inadequate for applying to a polymer blend]

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the Kushigata copolymer which can remove the above faults, it is the amount of giant molecules, and comonomer distribution of a polymer chain is uniform, fits the compatibilizer of a polymer blend, and can moreover be manufactured by the productive approach.

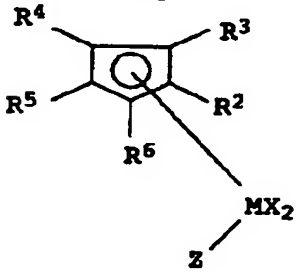
[Translation done.]

MEANS

[Means for Solving the Problem] We found out that such a technical problem was attained according to the manufacturing method of the Kushigata polymer which carries out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to the bottom of existence of one or more sorts of monomers b and the metallocene catalyst which were chosen from the long-chain 1-(C20-C40) alkene and the macro monomer. Moreover, we found out the approach of using the Kushigata polymer which is made to carry out copolymerization of one or more sorts of monomers a chosen from olefin partial saturation C2 - C18 hydrocarbon and the vinyl aromatic compound to the bottom of existence of one or more sorts of monomers b and the metallocene catalyst which were chosen from the long-chain 1-(C20-C40) alkene and the macro monomer, and is obtained, and the Kushigata polymer as a compatibilizer of a polymer blend, and the polymer blend containing the Kushigata polymer.
[0007] A new Kushigata polymer has at least one principal chain of the limited die length which branches many side chains preferably.
[0008] In a new manufacturing method, such a Kushigata polymer carries out copolymerization of the monomer a which forms the principal chain of a new Kushigata polymer generally, and the long-chain monomer b which forms a side chain generally to the bottom of existence of a metallocene catalyst, and is obtained.
[0009] Using a metallocene catalyst, Monomers a are all monomers in which a polymerization is possible, and have the carbon-carbon double bond especially the vinyl, or the vinylidene mold of an end preferably.
[0010] the suitable monomer a -- annular -- or -- desirable -- a line -- they are olefin partial saturation [which has structure] C2 - C18 hydrocarbon, and C8 - C16 vinyl aromatic compound. the example of C2 - C18 hydrocarbon -- a line or annular C2 - C18 monomer and a line or annular C4 - C -- it is diene preferably 18 polyene.
[0011] Suitable olefin unsaturated hydrocarbon is 1-(C2 - C10) alkene, for example, ethylene, a propylene, 1-butene, isobutene, 1-hexene, 1-octene, 1-decene, cyclopentene, a cyclohexene, cyclooctane, norbornene, 1,3-butadiene, 1, 5-cyclo-octadiene, norbornadiene, 5-vinyl-2-norbornene, 5-phenyl-2-norbornene, and dimethano octahydro naphthalene.
[0012] The very desirable monomers a are ethylene, a propylene, 1-butene, 1-hexene, and norbornene.
[0013] The examples of a suitable vinyl aromatic compound are styrene, alpha methyl styrene, a divinylbenzene, and 2-vinyl naphthalene.
[0014] The desirable vinyl aromatic series monomer a is styrene.
[0015] Of course, the monomer a of a publication can also be used as mixture for copolymerization, and is not criticality-like [a mixing ratio] in this case. desirable mixture -- the monomer of a propylene and others of Group a -- it is mixture with ethylene, 1-butene, 1-hexene, 1-octene, or norbornene preferably.
[0016] However, the very desirable only monomer a is used for composition of a polymer principal chain, and especially a propylene is used as a monomer a.
[0017] Monomer a and copolymerization under existence of a metallocene catalyst are possible

for the suitable monomer b. Such a monomer has the thing of the carbon-carbon double bond of an end especially vinyl, or a vinylidene mold preferably. Generally the description which distinguishes Monomer b from Monomer a is the chain length or polymerization degree. Monomer b is usually the amount of macromolecules from Monomer a. Preferably, the molecular weight Mn of Monomer b is 3 to 2000 times as large as Monomer a.
[0018] The suitable monomer b is long-chain C 20 - C40 monoolefin, for example, 1-ray KOSEN.

[0019] However, especially the desirable monomer b consists of macro monomers, i.e., a monomer, and are the chain end section which can copolymerize functionality, and oligomer which has end vinyl or a vinylidene radical preferably.
[0020] The monomer used as the foundation of a macro monomer may be chosen from Monomer a. Although a macro monomer may be the gay oligomer or co-oligomer of these monomers, it is gay oligomer preferably. The polymerization of the desirable monomer used as the foundation of a macro monomer is carried out by a cation or the living polymerization by which anion initiation is carried out. so, the suitable monomer b -- vinyl aromatic hydrocarbon — they are styrene or alpha methyl styrene, 2-vinyl naphthalene, 1,3-butadiene, an isoprene, and an isobutylene preferably.
[0021] Isobutylenes are Polymer(s), such as J.P.Kennedy. A polymerization is carried out by living cationic polymerization and molecular weight 300-50000 and the polyisobutylene which has 1000 - 20000 g/mol preferably are usually produced so that it may be indicated after six volumes (1995) and 579 page. Thus, generally molecular-weight-distribution Mw/Mn of the polyisobutylene obtained is 1.05-2.0. The initiator to be used is 2-chloro. - You may be a 2, 4, and 4-trimethyl pentane, and a living polymerization object is made to usually react with the arylsilane as an organic-functions-ized agent for introducing a partial saturation end group, for example, an allyl compound trimethyl silane.
[0022] Styrene is indicated after M.Swarc, J.Am.Chem.Soc., 78 volumes, (1956), and 2656 page. A polymerization is usually carried out by living anionic polymerization by making for example, n-butyl lithium or sec.-butyl lithium into an initiator, and a polystyrene anion is generated. subsequently, a living polymer chain -- general -- molecular weight 300-Mn 50000 -- it has 1000 - 20000 g/mol and molecular-weight-distribution Mw/Mn 1.05-1.5 preferably, and is generally organic-functions-ized in the chain end section. For this reason, a living polystyrene anion is made to react generally with an electrophilicity allyl compound, a vinyl compound, for example, an allyl chloride, or chlorination vinylbenzyl.
[0023] average molecular weight Mw and Mn list -- molecular-weight-distribution Mw/Mn — general -- elevated-temperature gel permeation chromatography (GPC) -- in 135 degrees C, it measures by law by the 1,2,4-trichlorobenzene which has polystyrene as a reference material. A new polymerization method is enforced under existence of a metallocene catalyst. A metallocene catalyst means the catalytic activity transition-metals compound which has at least one sort of ligands drawn from at least one sort of cyclopentadienyl ligands, or a cyclopentadienyl structural unit. Usually, a catalyst contains the compound which forms a metallocene cation and this compound is also called cocatalyst.
[0024] Especially the suitable metallocene complex used as the foundation of a metallocene catalyst is Formula III. [0025]
[Formula 9]

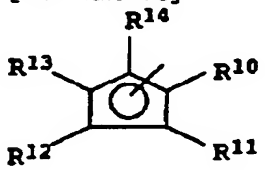


III

(M is titanium, a zirconium, a hafnium, vanadium, niobium, or a tantalum among a formula. X)

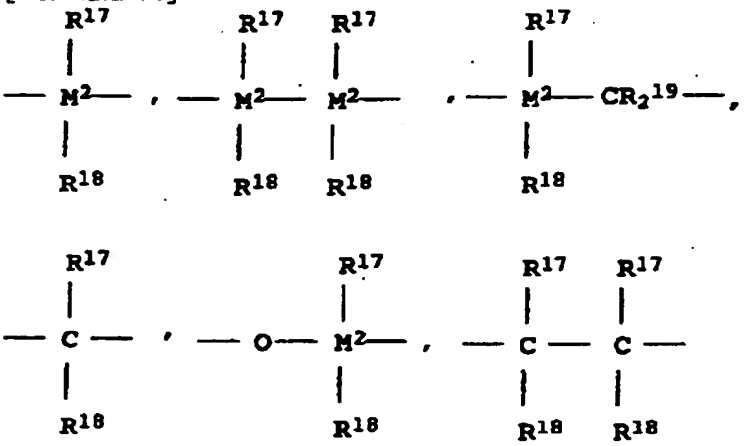
Fluorine, chlorine, a bromine, iodine, hydrogen, C1 - C10 alkyl, C6 - C15 aryl, the alkyl aryl and -OR7 which have 6-20 carbon atoms in an alkyl group at 1-10 carbon atoms and an aryl group Or -NR seven R8 it is -- R7 And R8 Respectively C1 - C10 alkyl, C6 - C15 aryl, alkyl aryl, They are arylated alkyl, fluoro alkyl, or fluoro aryl. each radical -- an alkyl group -- 1-10 carbon atoms and an aryl group -- 6-20 carbon atoms -- having -- R2 -R6 Respectively Hydrogen, C1 - C10 alkyl, the cycloalkyl of 5 - 7 member (you may have C1 - C10 alkyl as a substituent), C6 - C15 aryl or arylated alkyl (two contiguity radicals may form the annular radical of the saturation of 4-15 carbon atoms, or partial saturation together), or Si (R9)3 it is -- R9 C1 - C10 alkyl, C3 - C10 cycloalkyl, or C6 - C15 aryl -- it is -- Z -- X -- or [0026]

[Formula 10]



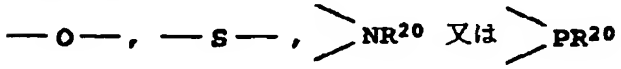
Come out and it is. R10-R14, respectively Hydrogen, C1 - C10 alkyl, The cycloalkyl of 5 which may have C1 - C10 alkyl as a substituent - 7 members, C6 - C15 aryl or arylated alkyl (two contiguity radicals may form the annular radical of the saturation of 4-15 carbon atoms, or partial saturation together), or Si (R15)3 it is -- R15 -- C1 - C10 alkyl, C6 - C15 aryl, or C3 - C10 cycloalkyl -- it is -- R5 [or] and Z -- together -- radical-R16-A- forming -- R16, [0027]

[Formula 11]



= BR17, =AlR17, -germanium-, -Sn-, -O-, -S-, It is SO, =SO2, =NR17, =CO, =PR17, or =P(O) R17. = R17, R18, and R19 the same -- or -- differing -- respectively -- hydrogen, a halogen, and C1-C -- 10 alkyl C1 - C10 fluoro alkyl, C6 - C10 fluoro aryl, C6 - C10 aryl, C1 C10 alkoxy **C2 - C10 alkenyl, Two contiguity radicals form a ring together with [are C7 - C40 arylated alkyl, C8 - C40 aryl alkenyl, or C7 - C40 alkyl aryl or] the atom which combines them, and it is M2. It is silicon, germanium, or tin and is A, [0028]

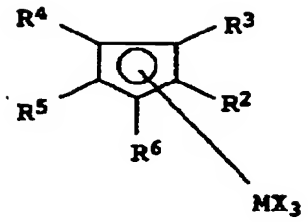
[Formula 12]



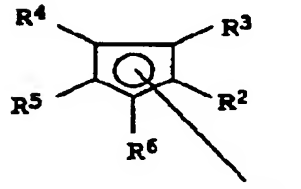
coming out -- it is -- R20 -- C1 - C10 alkyl, C6 - C15 aryl, C3 - C10 cycloalkyl, alkyl aryl, or Si (R21)3 it is -- R21 hydrogen, C1 - C10 alkyl, C6 - C15 aryl (C1 -C4 alkyl may permute), or C3 - C10 cycloalkyl -- it is -- R5 [or] R13 [and] -- together -- radical-R16- forming -- it is the metallocene complex expressed.

[0029] Inside of the metallocene complex of Formula III, [0030]

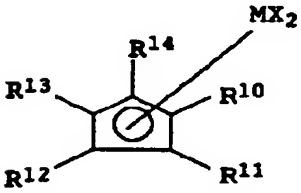
[Formula 13]

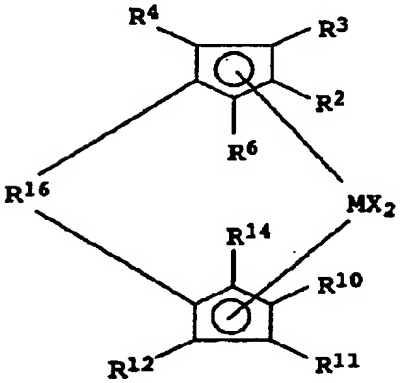


IIIa

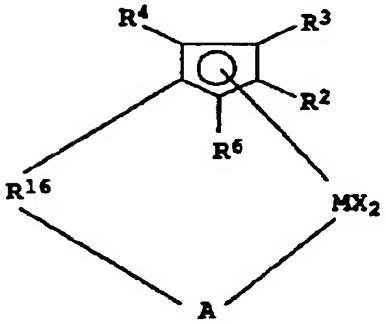


IIIb,





IIIc 及び



IIId

** -- it is desirable.

[0031] that in which especially a desirable transition metal complex contains as a ligand two aromatic ring systems over which the bridge was constructed mutually -- that is, it is especially the transition metal complex of Formulas IIIc and IIId.

[0032] The same thing is desirable although it is that Radical X is the same or a different thing.

[0033] M of especially the desirable compound of Formula IIIa is titanium, a zirconium, or a hafnium, and X is chlorine, and C1 - C4. It is alkyl or phenyl and is R2 -R6. They are hydrogen, or C1 - C4, respectively. It is alkyl.

[0034] especially the desirable compound of Formula IIIb -- M -- titanium, a zirconium, or a

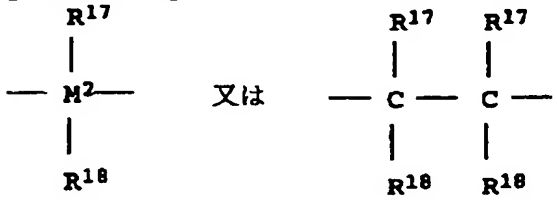
hafnium -- it is -- X -- chlorine, and C1 - C4 alkyl or phenyl -- it is -- R2 -R6 respectively -- hydrogen, and C1 - C4 Alkyl or Si (R9)3 it is -- R10-R14 -- hydrogen, and C1 - C4 Alkyl or Si (R15)3 it is -- it is a thing.

[0035] Especially the suitable compound of Formula IIIb has the same cyclopentadienyl group.

[0036] : in which especially the example of a suitable compound contains the following -- they are screw (cyclopentadienyl) zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, screw (methylcyclopentadienyl) zirconium dichloride, screw (ethylcyclopentadienyl) zirconium dichloride, screw (n-butylcyclopentadienyl) zirconium dichloride, bis (trimethylsilylcyclopentadienyl)zirconiumdichloride, and a corresponding dimethyl zirconium compound.

[0037] Especially the suitable compound of Formula IIIc is R2. R10 [and] It is the same, is hydrogen or C1 - C10 alkyl, respectively, and is R6. R14 [and] It is the same and they are hydrogen, methyl, ethyl, isopropyl, or tert.-butyl, respectively. R4 R12 [and] -- respectively -- C1 - C4 Alkyl and R3 R11 [and] -- respectively -- one [hydrogen or two contiguity radicals, and] R3 And R4 the annular radical to which R11 and R12 of another side have 4-12 carbon atoms together in a list -- forming -- R16, [0038]

[Formula 14]

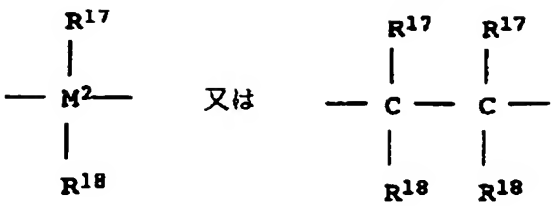


Come out, it is, M is titanium, a zirconium, or a hafnium, and X is chlorine, and C1 - C4. They are alkyl or phenyl.

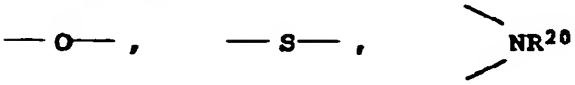
[0039] : in which especially the example of a suitable complex compound contains the following -- dimethylsilane diyl screw (cyclopentadienyl) zirconium dichloride -- Dimethylsilane diyl screw (indenyl) zirconium dichloride, Dimethylsilane diyl screw (tetrahydro indenyl) zirconium dichloride, Ethylene screw (cyclopentadienyl) zirconium dichloride, ethylene screw (indenyl) zirconium dichloride, Ethylene screw (tetrahydro indenyl) zirconium dichloride, Tetramethyl ethylene-9-fluorenyl cyclopentadienyl zirconium dichloride, Dimethylsilane diyl screw (3-tert.-butyl-5-methylcyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (3-tert.-butyl-5-ethylcyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (2-methyl indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-isopropyl indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-tert.-butyl indenyl) zirconium dichloride, Diethylsilane diyl screw (2-methyl indenyl) zirconium jib ROMIDO Dimethylsilane diyl screw (3-methyl-5-methylcyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (3-ethyl-5-isopropyl cyclopentadienyl) zirconium dichloride, Dimethylsilane diyl screw (2-methyl indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-methyl bends indenyl) zirconium dichloride, Dimethylsilane diyl screw (2-ethyl bends indenyl) zirconium dichloride, Methylphenyl silane diyl screw (2-ethyl bends indenyl) zirconium dichloride, Methylphenyl silane diyl screw (2-methyl bends indenyl) zirconium dichloride, Diphenyl silane diyl screw (2-methyl bends indenyl) zirconium dichloride, They are diphenyl silane diyl screw (2-ethyl bends indenyl) zirconium dichloride, dimethylsilane diyl screw (2-methyl indenyl) hafnium dichloride, and a corresponding dimethyl zirconium compound.

[0040] M of especially the suitable compound of Formula IIId is titanium or a zirconium, and X is chlorine, and C1 - C4. It is alkyl or phenyl and R16 , [0041]

[Formula 15]

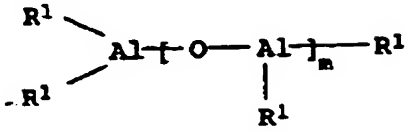


Come out, and it is and is A, [0042]
[Formula 16]

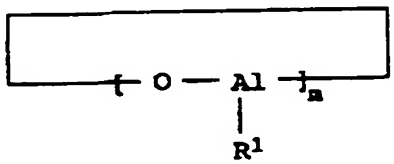


Come out, and it is and is R2 -R4. And R6 Hydrogen, C1 - C10 alkyl, C3 - C10 cycloalkyl, C6 - C15 aryl, Si (R9)3, or two contiguity radicals form the annular radical of 4-12 carbon atoms, respectively.
[0043] the cyclic hydrocarbon which could perform composition of such a complex compound by the well-known approach, and was permuted suitably -- Anio -- a reaction with the halogenide of Inn, titanium, a zirconium, a hafnium, vanadium, niobium, or a tantalum is desirable.
[0044] The example of a suitable manufacturing method is divided and is indicated by J.Organometal.Chem.369 (1989), and 359-370.
[0045] The mixture of a different metallocene complex may be used.
[0046] The catalyst manufactured according to a new manufacturing method contains a meta-ROSENIUMU ion formation compound as further component.
[0047] A suitable meta-ROSENIUMU ion formation compound is an ion compound which has Broensted acid as the ion compound and cation which have strong, neutral Lewis acid and a Lewis acid cation.
[0048] Strong, neutral desirable Lewis acid A formula IVM 3X1X2X3 IV (it is B preferably the inside of a formula, and M3 -- the III main-group element of a periodic table -- especially -- B, aluminum, or Ga -- X1, X2, and X3) Respectively Hydrogen, C1 - C10 alkyl, C6 - C15 aryl, Alkyl aryl, arylated alkyl, halo alkyl, or halo aryl (each radical has 6-20 carbon atoms in an alkyl group at 1-10 carbon atoms and an aryl group), or fluorine, chlorine, a bromine or iodine, especially halo aryl -- desirable -- pentafluorophenyl -- it is -- it is the compound expressed.
[0049] especially the compound of the desirable formula IV -- X1 and X2 And X3 the same thing -- it is tris (pentafluorophenyl) borane preferably.
[0050] The suitable ion compound which has a Lewis acid cation is formula V[(Ya+) Q1 Q2... Qz] d+ V (Y is the element of the I-VI main group of a periodic table, or an I-VIII vice-group among a formula Q1 -Qz) The radical which has a respectively single negative charge, for example, C1 - C28 alkyl, C6 - C15 aryl, alkyl aryl, arylated alkyl, halo alkyl, or halo aryl (each radical has 1-28 carbon atoms in an aryl group at 6-20 carbon atoms and an alkyl group), C1 - C10 cycloalkyl which may be permuted by C1 - C10 alkyl group, or -- although are a halogen, C1 C28 alkoxy **C6 - C15 aryloxy, silyl, or mel KAPUCHIRU, a is the integer of 1-6, z is the integer of 0-5 and d is equivalent to difference a-z -- d -- 1 -- stride -- 1 -- being equal -- it is the compound expressed.
[0051] A carbonium cation, an oxonium cation, a sulfonium cation, and especially a cation transition metal complex are suitable. A triphenylmethyl cation, silver cation and 1, and 1'-dimethyl ferro SENIRU cation is a special example. these have the opposite ion of non-coordination preferably, and are indicated by especially the PCT international public presentation WO 91/No. 09882 -- as -- a boron compound -- it is tetrakis (pentafluorophenyl) borate preferably.
[0052] The Broensted acid as a cation and the ion compound which has the opposite ion of non-coordination preferably are indicated by the PCT international public presentation WO 91/No. 09882, and a desirable cation is N and N-dimethyl anilinium.
[0053] Especially suitable meta-ROSENIUMU ion formation compounds are Formulas I or II.
[0054]

[Formula 17]



I



II

(-- the inside of a formula, and R1 -- C1 -C4 alkyl -- desirable -- methyl or ethyl -- it is -- m -- 5-30 -- it is the integer of 10-25 preferably --) -- they are the letter of opening and closing expressed, or an annular aluminoxane compound.

[0055] Manufacture of such aluminoxane compound oligomer makes a trialkylaluminium solution and water usually react. This divides and is indicated by the Europe patent application public presentation No. 284708 and U.S. Pat. No. 4,794,096.

[0056] Generally, aluminoxane compound oligomer exists as mixture of the line and annular chain molecule with which chain length differs. So, m can be called average. the metal alkyl of others [compound / aluminoxane] -- you may be mixture with alkylaluminum preferably.

[0057] Furthermore, aryloxy aluminoxane (U.S. Pat. No. 5,391,793 publication), amino aluminoxane (U.S. Pat. No. 5,371,260 publication), amino aluminoxane hydrochrolide (the Europe patent application public presentation No. 633264 publication), silyloxy aluminoxane (the Europe patent application public presentation No. 621279 publication), or such mixture may be used as a meta-ROSENIUMU ion formation compound.

[0058] Especially desirable metallocene complexes are ethylene screw (indenyl) hafnium dichloride and dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride. Very desirable metallocene catalysts are ethylene (bis-indenyl) hafnium dichloride / methyl aluminoxane, and dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride / methyl aluminoxane catalyst.

[0059] the new manufacturing method of the Kushigata polymer by this invention -- generally -- 50-300 degrees C -- desirable -- 0-150 degrees C -- especially -- 0-100 degrees C, and 0.01-3000 -- desirable -- 0.1-100 -- it carries out by 0.1-50 bars especially.

[0060] A polymerization can be performed by the solution, suspension, the liquid monomer, or the gaseous phase. A polymerization is preferably performed by the solution or the liquid monomer. The suitable solvent of solution polymerization is aliphatic series or an aromatic series organic solvent, and this may be halogenated. Toluene, ethylbenzene, a chlorobenzene, and a heptane are mentioned as an example.

[0061] A new polymerization method can be performed with a continuous magnetization method or a batch method. many stirring iron pots (reaction machine cascade) by which the suitable reaction machine was connected including the consecutive operation type stirring iron pot -- a tubular reaction machine or a loop-formation-like reaction machine is also still more possible.

[0062] The ratio of the monomer a opposite monomer b under polymerization is not criticality-like. general -- the mole ratio of the monomer a whole-quantity pair monomer b whole quantity -- 0.1-100 -- it is preferably chosen as 1-50.

[0063] the invert ratio of Monomer b -- usually -- 1-100 -- it is 5 - 90 % of the weight preferably. the rate of Monomer b that the chemical bond of [in a new Kushigata polymer] was carried out asks for the area under the curve obtained to the Kushigata polymer by the elevated-temperature gel-permeation-chromatography method as compared with the area of the homopolymer standard substance -- having -- 0.5-90 -- it is 5 - 75 % of the weight preferably.

[0064] the average molecular weight Mw and Mn list of a new Kushigata polymer -- molecular-weight-distribution Mw/Mn -- general -- elevated-temperature gel permeation chromatography (GPC) -- it asks at 1,2,4-trichlorobenzene and 135 degrees C by law, using polystyrene as a

reference material.
[0065] the average molecular weight Mw of a new Kushigata polymer -- generally -- 5000-1 million -- it is 10000 - 500000 g/mol preferably. molecular-weight-distribution Mw/Mn of a new copolymer -- usually -- 1.4-10 -- it is 1.4-3 preferably.
[0066] the glass transition temperature from which the melting point is 80-155 degrees C preferably, and one glass transition temperature or a large number usually separated 20-160 degrees C of new Kushigata polymers -100-250 degrees C of two separated glass transition temperature are -70-100 degrees C (it measures by the differential scanning calorimetry and DSC) preferably.
[0067] A very desirable new Kushigata polymer has one of the side chains of a polypropylene principal chain and polystyrene, or a polyisobutylene. the molecular weight Mw of this copolymer -- 5000-1 million -- desirable -- the molecular weight Mn of 10000 - 500000 g/mol and a side chain -- 500-50000, and the molecular weight distribution of a macro monomer that serve as a foundation of 2000 - 20000 g/mol and a side chain preferably -- usually -- 1.05-2.0 -- it is 1.05-1.4 preferably. the number of graft branching which the side chain of the Kushigata polymer reached comparatively and was calculated from the total molecular weight Mn of a desirable new Kushigata polymer -- the rate of 0.05-50, the macro monomer polystyrene by which is 1-20 preferably and the chemical bond was carried out, or a polyisobutylene -- 0.5-90 -- it is 5 - 75 % of the weight preferably.
[0068] The desirable new Kushigata polymer which has the side chain of a polypropylene principal chain and polystyrene, or a polyisobutylene usually has 120-155 degrees C and the glass transition temperature of -70-100 degrees C preferably the melting point of 100-160 degrees C.
[0069] Furthermore, although a new Kushigata polymer contains sheep inversion monomer b5-50 % of the weight to the total amount of polymers, it is desirable that Monomer b is not included substantially.
[0070] A new Kushigata polymer is applicable to the polymer blend which consists of two or more sorts of components as a compatibilizer. All polymers, i.e., thermoplastics resin, for example, polyolefine, polystyrene, a polyamide, polyester, a polycarbonate, polyvinyl chloride and an elastomer, for example, a polyisobutylene, polybutadiene, and polyisoprene can be used as a component of a polymer blend in principle. A new Kushigata polymer is used in favor of the polymer blend containing the polymer blend containing a nonpolar hydrocarbon polymer especially an olefin polymer, and polyvinyl aromatic series. Suitable polyolefine is the homopolymer of a propylene, a copolymer, or a polyisobutylene at a polyethylene mold like HDPE, LLDPE, or LDPE, and a pan. To this contractor, it is well-known, for example, these polymers are Ullmann's. Encyclopedia of Industrial It is indicated by Chemistry, 21 volumes, 487-577 pages, and VCH (1992). The special example of polyvinyl aromatic series is the homopolymer or copolymer of styrene well-known to this contractor, or alpha methyl styrene similarly. What has the side chain of a new Kushigata polymer especially a polypropylene principal chain and polystyrene, or a polyisobutylene is especially used for the polymer blend containing a propylene polymer especially a propylene homopolymer and a styrene polymer, especially a styrene homopolymer preferably.
[0071] The ratio of the basic polymer of a polymer blend is not criticality-like generally. the case of the polymer blend containing a propylene polymer and a styrene polymer -- a ratio -- 1-99 -- it is 5 - 20 % of the weight preferably. [for example,]
[0072] In the blend which consists of a polymer blend especially a propylene polymer, and a styrene polymer, although it has the side chain of a new Kushigata polymer especially a polypropylene principal chain and polystyrene, or a polyisobutylene, a content is not criticality-like. it -- the whole quantity of a basic polymer -- receiving -- usually -- 0.001-50 -- it is 0.2 - 20 % of the weight preferably.
[0073] Furthermore, a new polymer blend can contain the amount of common use of the usual additive known in PURASUCHIKUSU industry.
[0074] Generally a new Kushigata polymer brings about the improvement of whenever [rigidity / of the test piece especially created from the new polymer blend /, tensile strength, and/or

breaking extension].

[Translation done.]

EXAMPLE

(Example)
A) Styrene 19.4ml (169mmol) newly distilled to styrene 18ml (157mmol) and the macro monomer SO which were newly distilled to manufacture desiccation toluene 200ml of a styrene macro monomer and the macro monomer SI which have the manufacture example 1 end vinyl group of a macro monomer was introduced into the desiccation flask washed by the argon style.
[0076] Subsequently, several drops of 2M toluene solutions of sec.-butyl lithium were added at 25 degrees C until the thin color would be in the stable state. Then, 2ml of initiator solutions was added.
[0077] Mixture was cooled at -78 degrees C 1 hour after, and it diluted with THF100ml. and toluene 100ml similarly cooled by -78 degrees C in the living poly anion solution -- it added in 7ml (80mmol) of inside allyl bromides, and the solution of THF100ml.
[0078] The 16.3g polystyrene SI (Mn=4000 g/mol, Mw/Mn=1.08) completely formed into allyl compound organic functions and 17.5g SO were obtained.
[0079] The property of the generated styrene macro monomer is shown in Table 1.
[0080] The manufacture desiccation flask of the isobutylene macro monomer which has an example 2 end vinyl group was washed by the argon style, and 250ml [of desiccation methylene chlorides], 2, and 2'-bipyridyl 0.75g (4.5mmol) and desiccation n-hexane 350ml were introduced. Subsequently, mixture was cooled at -78 degrees C.
[0081] After 12ml (0.11 mols) of titanium tetrachlorides, and 5 minutes, 2in 6ml of methylene chlorides-chloro - 10ml (2, 4, and 4-trimethyl pentane 1.5g and n-hexane 9ml (6.75mmol)) of solutions was added. Then, 71ml (51.3g) was dropped to isobutene 44ml (31.7g) and the macro monomer IBII to the macro monomer IBI.
[0082] after [10 minutes] and allyl compound trimethyl silane 5g (43mmol) -- adding -- further -- methanol 50ml was added after 30 minutes.
[0083] 31g Polyisobutylene IBI (Mn=4700 g/mol, Mw/Mn=1.16) and the 50g macro monomer IBII which were completely formed into allyl compound organic functions were obtained after processing.
[0084] The property of the generated isobutylene macro monomer is shown in Table 1.
[0085]
[Table 1]
表1：

末端ビニル基を有するポリスチレンおよびポリイソブチレンのマクロモノマー

記号[a]	M_n (g/mol)	M_w (g/mol)	M_w/M_n	末端基	官能価 (%)
SO	4300	4600	1.06	ビニルベンジル[b]	> 95
SI	4000	4400	1.08	アリル	> 95
IBI	4700	5500	1.16	アリル	> 95
IBII	7600	9300	1.23	アリル	> 95

a) S= polystyrene macro monomer IB= polyisobutylene macro monomer b PSLi is made to react with chlorination vinylbenzyl and it is Composition c. The end group functional value of a polystyrene macro monomer measured and asked for the signal reinforcement of an end double bond proton, and the signal reinforcement of the methyl proton of the initiator radical of a chain start point by 1 H-NMR spectroscopy.

[0086] B) The 0.5l. reactor of the propylene and styrene macro monomer under existence of the manufacture example 3 dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride / methyl aluminoxane of a new Kushigata polymer which carried out copolymerization desiccation was washed by the argon style, and was filled with 20-degree C desiccation toluene 200ml.

[0087] Then, 1.9ml (equivalent to aluminum of 3.3mmol and molar mass 1000 g/mol by cryoscopic-method measurement) of toluene solutions of methyl aluminoxane and macro monomer SI2.5g (equivalent to 0.625mmol) subsequently to desiccation toluene 50ml dissolved were added with the argon gage pressure of 0.3 bars.

[0088] The dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride dissolved in 1ml of toluene solutions of methyl aluminoxane was put for 2 hours, preliminary activation was carried out, and it added behind. Refer to Table 2 for the amount of metallocene chloride. Then, it decompressed, the argon was removed and propene ** was set as 0.1 bars. By suitable propene supply, the pressure under polymerization was held to 0.1 bars, and temperature was held at 20 degrees C.

[0089] It obtained with the yield which shows the Kushigata polymer in Table 2.

[0090] An experimental result is shown in Table 2.

[0091]

[Table 2]

表 2:

ポリプロピレン主鎖およびポリスチレングラフト鎖を有するグラフト共重合体

記号[a]	メタロセン濃度 *10-5, (mol/l)/ (メタロセンジクロリド (mg))]	マクロモノマー 転化率 (%)	マクロモノマー 含有量[b] (重量%)	M_w (kg/mol)	M_w/M_n	グラフト鎖数 n_g/ 分子	M_{nPP}[c] (kg/mol)	T_m (°C)	収量 [g]
GSO[d]	3.3 (4.2)	> 85	7	13.6	2.6	0.085	5	-	4.4
GSI1	4 (5.8)	24.3	7	310	2.46	2.1	41	153.4	5.6
GSI2	2 (2.9)	49.4	20	158	2.16	3.5	16	151.9	8.9
GSI3	8 (11.6)	34.7	40	44.1	1.44	2.9	8	144.4	3.5
GSI4	2 (2.9)	26.2	72	22.6	1.4	2.84	4	122.2	3.0

a) 記号：G＋マクロモノマーの記号＋試料No.

b) グラフト共重合体中のポリスチレン含有量

c) 2つのグラフト鎖間のポリプロピレン列の平均分子量

$M_{nPP} = (M_{n\,全体} - n_g * M_{n\,マクロモノマー})/(n_g + 1)$

d) 触媒系エチレンビス（インデニル）ハフニウムジクロリド／メチルアルミノキサン、重合温度50℃、SOマクロモノマー0.85g（表1参照）

[0092] The 0.5l. reactor of the propylene and isobutylene macro monomer under existence of example 4 dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride / methyl aluminoxane which carried out copolymerization desiccation was washed by the argon style, and was filled with 20-degree C desiccation toluene 200ml.

[0093] Then, 8.3g (equivalent to 1.09mmol) of 1.9ml (equivalent to aluminum of 3.3mmol and molar mass 1000 g/mol by cryoscopic-method measurement) of toluene solutions of methyl aluminoxane and the macro monomer IBII subsequently to desiccation toluene 50ml dissolved was added with the argon gage pressure of 0.3 bars.

[0094] 2.9mg of the dimethylsilane diyl screw (2-methyl -4, 5-bends indenyl) zirconium dichloride dissolved in 1ml of toluene solutions of methyl aluminoxane was put for 2 hours, preliminary activation was carried out, and it added behind.
[0095] Then, it decompressed, the argon was removed and it was set as 0.15 bar of propene **.
[0096] By suitable propene supply, the pressure under polymerization was held to 0.15 bars, and temperature was held at 20 degrees C.
[0097] 12.0g of a copolymer GIBII1 was obtained.
[0098] The copolymer GIBII2 was similarly manufactured by 0.1-bar propene **.
[0099] Furthermore, the copolymer GIBI1 was manufactured by 0.2 bar of propene ** using 12.8g (2.7mmol) of the macro monomer IBI, and the copolymer GIBI2 was manufactured by 0.1 bar of propene **. Furthermore, for details, refer to Table 3.
[0100] An experimental result is shown in Table 3.
[0101]
[Table 3]

表 3:

ポリプロピレン主鎖およびポリイソブチレングラフト鎖を有するグラフト共重合体

記号 a)	プロペン圧 (bar)	マクロモノマー 転化率 (%)	マクロモノマー 含有量 b) (重量%)	M_w (kg/mol)	M_w/M_n	グラフト分枝数 n_g/分子	M_{nPP} c) (kg/mol)	T_m (°C)	収量 [g]
GIBI1	0.2	11.0	24	114	2.1	2.95	17	147.6	17.6
GIBI2	0.1	32.8	51	61	1.73	3.25	8	143.5	14.6
GIBII1	0.15	6.0	15	103	1.75	1.1	28	148.4	12.0
GIBII2	0.1	7.2	14	42	1.43	0.52	19	149.9	11.2

a) 記号：G＋マクロモノマーの記号＋試料No.

b) グラフト共重合体中のポリイソブチレン含有量

c) 2つのグラフト鎖間のポリプロピレン列の平均分子量

$$M_{nPP} = (M_{n全体} - n_g \cdot M_{nマクロモノマー})/(n_g + 1)$$

[0102] C) Manufacture gay polypropylene PS-S134 (Mw213000, Mn94000, Mw/Mn2.27) (it used as a basic polymer.) of polypropylene / polystyrene / Kushigata polymer blend Shell KF6100H (Mw324000, Mn72000, Mw/Mn4.5) and gay polystyrene Buna These were used by the ratio of 85 % of the weight of polypropylene, and 15 % of the weight of polystyrene.
[0103] The polypropylene principal chain and the polystyrene side chain, and the new Kushigata polymer with which standard polystyrene graft chain length has the content from which Mn4000** differs were manufactured like the example 3, and it was used in a various amount by

using this Kushigata polymer as a compatibilizer. Furthermore, for details, refer to Table 4.
[0104] The blend of a basic polymer and the Kushigata polymer was manufactured as follows.
[0105] Polypropylene and polystyrene were mixed in 180 degrees C by the ratio which had the granular thing calculated at the kneading room of the Brabender plastometer (content of 24g) for 15 minutes.
[0106] It adds to a suitable quantity of a compatibilizer, and is Irganox. 0.4 % of the weight of stabilizer mixture containing B225, J3025 (Ciba-Geigy make) 25%, and 50% of Jonol was beforehand added in the granular object.
[0107] The piece of a polymer blend blank test was manufactured, and the following quality of polymerization somatic was measured by the following approaches.
[0108]
It is ductility at the time of fracture by the tension test method of the tensile strength DIN 53455 by the tension test method of the elastic modulus DIN 53455 by the tension test method of DIN53455. [0109]
[Table 4]

表 4:

新規櫛形重合体で相溶化されたポリプロピレン／ポリスチレンブレンド85／15の機械的性質

記号	グラフト共重合体				ブレンドの性質		
	M_w (kg/mol)	グラフト鎖数／分子	ポリスチレン含有量 (%)	ブレンド中の割合 (%)	弾性率 (MPa)	σ_{max}a) (N/mm^2)	ε_{Rb}b) (%)
B10	-	-	-	0	1197	28.68	18.0
BG1	13.6	0.085	7	1	1300	31.80	10.5
BG2	13.6	0.085	7	3	1206	29.38	9.6
BG3	13.6	0.085	7	5	1181	32.12	8.7
BG4	310	2.1	7	1	1516	35.02	8.1
BG5	310	2.1	7	2.5	1472	36.02	6.2
BG6	310	2.1	7	4	1545	37.33	6.6
BG7	310	2.1	7	8	1564	38.63	4.6
BG8	158	3.5	20	1	1418	35.28	5.6
BG9	158	3.5	20	2.5	1476	39.78	6.4
BG10	44.1	2.9	40	0.5	1330	36.01	6.1
BG11	44.1	2.9	40	1.5	1274	36.79	7.3
BG12	22.6	2.84	72	1	1174	32.84	6.1

a) 引張強度　　b) 破断時伸度

[0110] The mere small quantity of the new Kushigata polymer compatibilizer under blend of bringing about the substantial increment in ductility at the time of rigidity, tensile strength, and fracture, for example, 1%, is clear. This showed the improvement of interphase adhesion and was found out by the morphological research using a scanning electron microscope.

[Translation done.]